#### Chemistry 1B

#### Fall 2016

Topic 23
[more] Chemical Kinetics



- kinetics and mechanism of chemical reaction
- energy profile and reaction coordinate
- activation energy and temperature dependence of rate constant
- catalysis

# chemical kinetics

elementary reactions reaction mechanisms reaction energy profile and the reaction coordinate diagram

#### have already covered worksheet 10 sections I-IV

Chemistry 1B-AL Fall 2016, Study Guide and Worksheet XI

#### Learning Objectives and Worksheet XII

#### Chemistry 1B-AL Fall 2016

Lectures (21-22 ) Che mical Kinetics

To date CHEM1B-AL has focused on the structure and chemical properties of atoms and
molecules. Chemical kinetics, the final topic of the course, shifts attention to chemical
reactions. In particular we will study how measuring the factors affecting the rate of a
chemical reaction gives clues to the series of individual steps, i.e. the mechanism, by which
the reaction proceeds.

ı.	Rasio	Сопсел	its and	Definitio	ПБ

	Basic Concepts and Definitions
1.	For a chemical reaction, what are the differences between the information that is provided by thermodynamics $[eq\ olimbia]$ (CHEM-1A, CHEM-1C) and kinetics?
2.	In a kinetics experiment one measures decreases inor increases in
	Y5
ı.	Differential rate laws
1.	The rate at which a reaction occurs is written in terms of the of the
	reactants (raised to powers) since for higher
	there are a greater number of molecular
	allowing the possibility that the reaction will proceed more
	rapid ly.
2.	In the differential rate expression:
	$-\frac{d[X]}{dt} = +n\frac{d[Y]}{dt} = k_{j}[A]^{m}[B]^{c} - k_{i}[C]^{c}[D]^{c}$
	i. $= \frac{d\{X\}}{dt}$ represents the of aX.

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	ii.	$\frac{d[Y]}{dt}$ represents the		of a		Y.
	iii.	$k_{_{\! f}}$ and $k_{_{\! f}}$ are the $\_$		_and		
			respectively.			
	iv.	the order of the above r		tant A is	_	
3.	Theexp	pression				
	$-\frac{d[A]}{dt}$	$\underline{a} = k_f [A]_0^m [B]_0^n$				
	describ	es the rate of reaction wh	ren		and th	us is called the
		г	atelaw. Heret	he total rate or	ter is	
4.	$If -\frac{d[x]}{dt}$	$\frac{A]}{f} = k_f [A]^m$ , the instanta	neous rate of i	eaction isgiven	by the	
	of a plo	ot of [A] vst.				
III.	Determi	ining order of a reaction				
1.	For a re	eaction all reactant conce	ntrations are k	ept constant ex	cept for [A] <sub>o</sub> .	
	i.	If The initial rate increas	es 9-fold when	[A] <sub>o</sub> is tripled (i	.e. [A] <sub>o</sub> increase	d 3-fold), the
		order of the reaction in [	[A] is	_		
	ii.	If the reaction was third	order in [A] an	d the concentra	ation of [A] <sub>o</sub> is o	oubled, the
		initial rate of reaction in	creases by a fa	ttor of		
	iii.	If the rate of reaction do	esn't change v	hen [A]₀ is dou	bled, the order	of the reaction
		in reactant A is				
2.	A react	ion has an initial reaction	rate (loss of [A	]) that is first-o	rder in [A] <sub>o</sub> an d	second-order
	in [B] <sub>0</sub> .	For the initial concentrati	ions of [A] <sub>o</sub> =1 f	M and [B]₀=2 M	the initial rate i	$S = \frac{20mol}{Lsec}$ .
	Therat	e constant for the reaction	n is			
IV.	Integrat	ed rate expressions				
1.	Whilet	the <b>differential</b> rate expre	ssion gives the		of the o	on centration
	of a rea	actant or product with		_ the integrate	d rate expression	on gives the
	total_		of 1	the reactant or p	product as a fur	iction of

2

#### this video and



#### : worksheet 10 sections I-VI and VII (6-10)

Chemistry 1B-AL Fall 2016, Study Guide and Warksheet XI

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2.	Since integral calculus is not a prerequisite for CHEM1B (however you better take this
	$important \ class !!), you \ will be given the formulas for the integrated rate \ expressions \ will be$
	supplied on your exams. However you should recognize:
	For the reaction where effectively only reactant [A] varies:
	al Al

$$-\frac{d[A]}{dt} = k[A]^x$$
i. for  $ln[A] = -kt + ln[A]_0$  the order  $x =$ 
ii. for  $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$  the order  $x =$ 
iii. for  $[A] = -kt + [A]_0$  the order  $x =$ 

3.		e integrated rate expression: for $lm[A] = -kt + lm[A]_0$ a plot of	vs	would be
		a straight line with slope		
	ii.	for $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$ a plot of	vs	would be a
		straight line with slope k		
	iii.	for $[A] = -kt + [A]_0$ a plot of	vs	would be a
		straight line with slope .		

# V. Kinetics and the mechanism of a chemical reaction In O-Chem and beyond you will be studying how different kinetic analyses are used to determine a variety of reaction mechanisms. In CHEM1B we will get a 'taste' of the process of kinetics → mechanism for a multi-step reaction but limit the playing field to one type of process- a slow initial step followed by a fast reaction. VI. Elementary reactions 1. An elementary reaction is one that corresponds to \_\_\_\_\_\_\_\_. 2. When the measured rate law for a chemical reaction does not correspond to the reaction stoich iometry the reaction is \_\_\_\_\_\_\_ an elementary reaction. When the measured rate law for a chemical reaction does not correspond to the reaction \_\_\_\_\_\_ an elementary reaction.

3.	An elementary reaction involving only the interaction (	(collision) between two reactants is
	and has a	order overall rate.
4.	An elementary reaction involving only decomposition	of a single reactant
	and has a	order overall rate.
5.	An elementary reaction that requires the improbable of	collision of three molecular species is a
	and is a	elementary reaction.
VII.	Temperature dependence of the rate constant	
1.	The Arrhenius equation is $k=zpe^{-E_{\gamma_{RT}}}$	
2.	The factor z is related to the	of the molecules
	participating in the reaction.	
3.	The magnitude of factor pidepends on how the reaction	on depends on the
	of the molecules interacting in the reaction.	
4.	The term $e^{-E_{\gamma_{RT}}}$ enters into the rate giving the relativ	ve
5.	At a given temperature a larger activation energy $E_{\alpha}$ wi	ill result in collisions
6	having  For a given activation energy E <sub>a</sub> a higher temperature 1	T will regult in
٠.	collisions having	
7.	A maxima in the reaction profile (energy vs extent of re	
	corresponds to the	
8.	The energy difference between the reactants and the	maximum isthe
9.	The energy difference between the products and the r	maximum is the
10.	. A relative minimum in the reaction profile is a	
VIII.	l. Catalysis	
1.	In general, a catalyst increases the rate of reaction by a	allowing a reaction pathway that
2.	What are three types of catalysis	
	i.	
	ii. 	
	iii.	

- elementary reactions
- kinetics and the mechanism of a chemical reaction
- energy profile and reaction coordinate

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$
 at T< 500K

if the reaction was a collision between a NO<sub>2</sub> molecule and a CO molecule one might expect for the differential rate law:

$$-\frac{d[NO_2]}{dt} = k[NO_2][CO]$$

but the observed rate of reaction is:

$$-\frac{d[NO_2]}{dt} = k[NO_2]^2$$

You might ask?



the observed kinetics 
$$-\frac{d[NO_2]}{dt} = k[NO_2]^2$$

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$
 at T< 500K

is not consistent with this stoichiometric equation in representing the actual molecular collisions involved in the reaction

ok?? but first let's look at reactions where the stoichiometric equation DOES represent the actual collision process, these are called

**ELEMENTARY REACTIONS** 



back to the question: so what's up DOC ??

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$
 at T< 500K

answer: the above (stoichiometric) equation NO<sub>2</sub> colliding with CO does NOT represent the molecular mechanism (molecular steps of the reaction)

in actuality: the reaction takes place in two steps

$$NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$$
 slow

net reaction

$$NO_3(g) + CO(g) \rightarrow CO_2(g) + NO_2(g)$$
 fast

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$
 overall reaction

$$NO_2(g) + NO_2(g) \xrightarrow{k_{S/OW}} NO(g) + NO_3(g)$$
 slow  $NO_3(g) + CO(g) \xrightarrow{k_{fast}} CO_2(g) + NO_2(g)$  fast

- The two steps are the actual molecular processes by which the reaction occurs and is the MECHANISM the reaction
- They represent ELEMENTARY reactions
- The combination of elementary reactions must sum to the overall stoichiometry
- Species [e.g. NO<sub>3</sub> (g)] appearing in the steps of the mechanism, but not the overall reaction are REACTION INTERMEDIATES

$$K_{slow}$$
 $NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$   $slow$ 
 $k_{fast}$ 
 $NO_3(g) + CO(g) \longrightarrow CO_2(g) + NO_2(g)$  fast

- rates for individual steps come directly from the stoichiometry of the ELEMENTARY reactions
- how to combine rates of elementary reactions to get overall rate equation LOTS OF TRICKS (but we don't have time for many)
- our ONE example will be slow reaction followed by rapid reaction (like above reaction)

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

T<500K

$$k_{S/OW}$$
 2 NO<sub>2</sub>(g)  $\xrightarrow{k_{S/OW}}$  NO(g) + NO<sub>3</sub> (g) slow

$$NO_3(g) + CO(g) \xrightarrow{k_{fast}} CO_2(g) + NO_2(g)$$
 fast

since these are ELEMENTARY reactions:

$$-\frac{d[NO_2]}{dt} = k_{slow}[NO_2]^2 = +2\frac{d[NO_3]}{dt} \quad \text{slow}$$
$$-\frac{d[CO]}{dt} = k_{fast}[NO_3][CO] \quad \text{fast}$$

- since k<sub>fast</sub> >> k<sub>slow</sub> as soon as slow reaction produces NO<sub>3</sub>
   the fast reaction occurs
- the total rate is the just the rate of the slow step total rate=  $k_{slow}$  [NO<sub>2</sub>]<sup>2</sup> (2<sup>nd</sup> order in NO<sub>2</sub>, 0<sup>th</sup> order in CO)

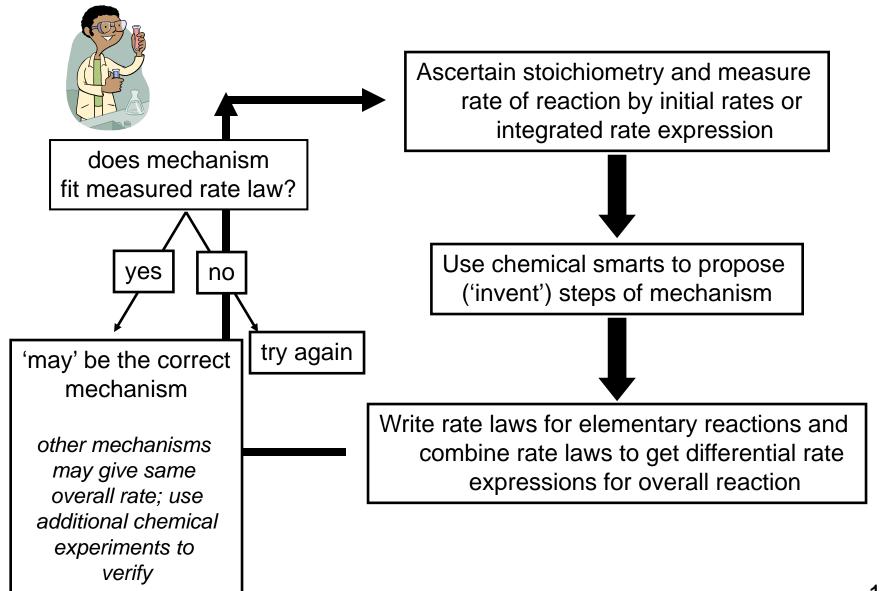


#### factoids about rate laws and mechanisms

- in general the rate law cannot be written in terms of the stoichiometric coefficients of the overall reaction
- the rate law for an elementary reaction IS determined by the molecularity (stoichiometry) of the individual step
- the overall rate law is obtained from combining rate laws of elementary reactions
- an overall reaction where the measured rate law and the stoichiometric coefficients 'match' MAY or MAY NOT be an elementary reaction

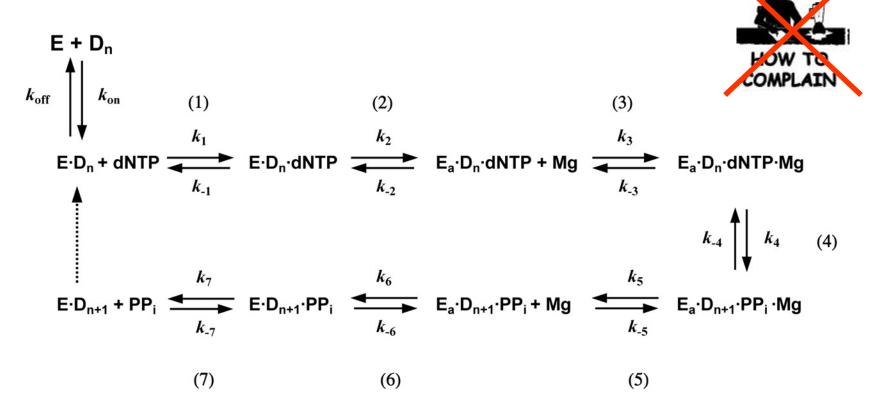


#### the actual process of determining mechanism of a reaction



#### DNA synthesizer kinetics

and your thought Chem 1B kinetics was complicated !!



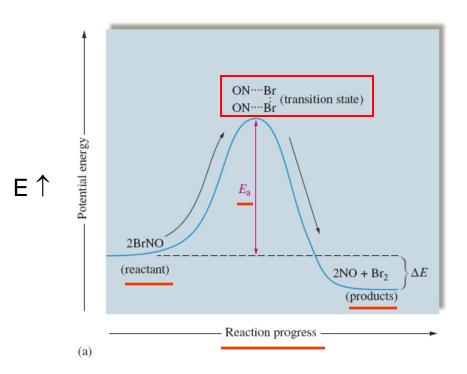
$$\begin{aligned} k_{\text{on}} &= 1.2 \times 10^7 \, \text{M}^{-1} \cdot \text{s}^{-1}, \ k_{\text{off}} &= 0.06 \, \text{s}^{-1}, \ k_{\text{1}} &= 1.25 \times 10^7 \, \text{M}^{-1} \cdot \text{s}^{-1}, \ k_{\text{-1}} &= \\ 250 \, \text{s}^{-1}, \ k_{\text{2}} &= 50 \, \text{s}^{-1}, \ k_{\text{-2}} &= 3 \, \text{s}^{-1}, \ k_{\text{3}} &= 9.5 \times 10^5 \, \text{M}^{-1} \cdot \text{s}^{-1}, \ k_{\text{-3}} &= 100 \, \text{s}^{-1}, \ k_{\text{4}} \\ &= 150 \, \text{s}^{-1}, \ k_{\text{-4}} &= 40 \, \text{s}^{-1}, \ k_{\text{5}} &= 100 \, \text{s}^{-1}, \ k_{\text{-5}} &= 9.5 \times 10^5 \, \text{M}^{-1} \cdot \text{s}^{-1}, \ k_{\text{6}} &= 4 \, \text{s}^{-1}, \ k_{\text{6}} &= 4 \, \text{s}^{-1}, \ k_{\text{7}} &= 60 \, \text{s}^{-1}, \ k_{\text{7}} &= 1.45 \times 10^4 \, \text{M}^{-1} \cdot \text{s}^{-1}. \end{aligned}$$

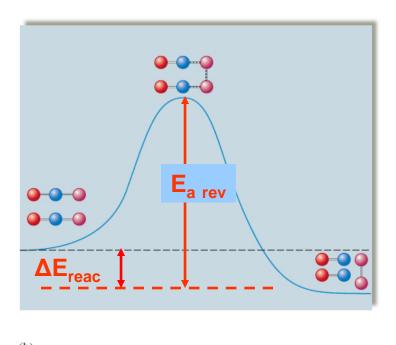


#### the reaction coordinate and course of a chemical reaction

#### elementary reaction 2BrNO → 2NO +Br<sub>2</sub>

### molecularity?

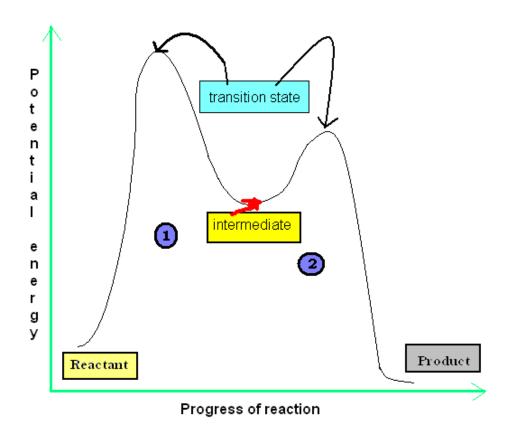




- energy vs reaction coordinate (progress of reaction reactants –products)
- transition state (maxima of E vs reaction coordinate)

[N---Br bonds breaking, Br---Br bond forming]

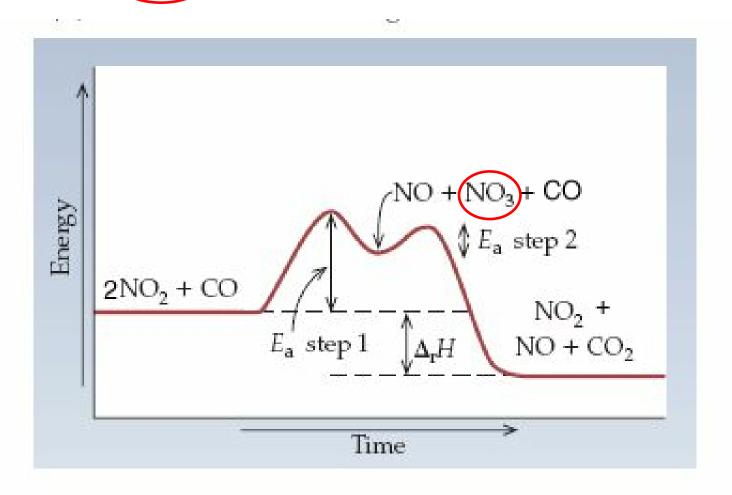
- activation energy (E<sub>a</sub>=E<sub>transition state</sub> E<sub>reactants</sub>)
- reverse activation energy (E<sub>a rev</sub>= E<sub>transition state</sub> E<sub>products</sub>)
- $\Delta E_{reaction}$  ( $\Delta H$ )= ( $E_{products} E_{reactants}$ )



('stable') **Reaction Intermediate** is at a relative minimum along curve

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$
 at T< 500K

$$NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$$
 slow  
 $NO_3(g) + CO(g) \longrightarrow CO_2(g) + NO_2(g)$  fast





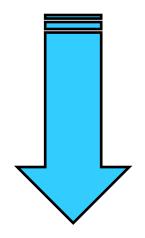


our last video !!





# onto more kinetics !!!



#### Zumdahl figure 15.8 $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

$$NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$$
 slow

Step 1



Step 2

$$NO_3(g) + CO(g) \rightarrow CO_2(g) + NO_2(g)$$
 fast



- an elementary reaction represents the molecules 'colliding' in an actual step of the overall reaction
- the rate law for an elementary reaction IS determined by the stoichiometry of the elementary reaction (the order of each reactant is its stoichiometric coefficient)
- the overall order of an elementary reaction is its molecularity
- the 'sum' of the individual elementary reactions must yield the equation for the overall reaction

#### elementary reaction

molecularity

$$-\frac{d\begin{bmatrix} {}^{14}C \\ {}^{6}C \end{bmatrix}}{dt} = k_1 \begin{bmatrix} {}^{14}C \\ {}^{6}C \end{bmatrix}$$
 first-order

unimolecular

$$O_{3}(g) + NO(g) \xrightarrow{k_{2}} O_{2}(g) + NO_{2}(g)$$

$$-\frac{d[O_{3}(g)]}{dt} = k_{2}[O_{3}][NO] \text{ second-order}$$

bimolecular

 $2Cl \bullet (g) + Cl_2(g) \xrightarrow{k_3} 2Cl_2(g)$   $-\frac{d[Cl_2(g)]}{dt} = k_3[Cl \bullet]^2[Cl_2] \text{ third-order}$ 

termolecular improbable



if 
$$A + 2B \rightarrow C$$
 **IS** an elementary reaction then

$$-\frac{d[A]}{dt} = k[A][B]^2 \qquad \text{termolecular}$$

**TRUE** 

if the measured rate law for A + 2B  $\rightarrow$  C is



$$-\frac{d[A]}{dt} = k[A][B]^2$$
 third order then

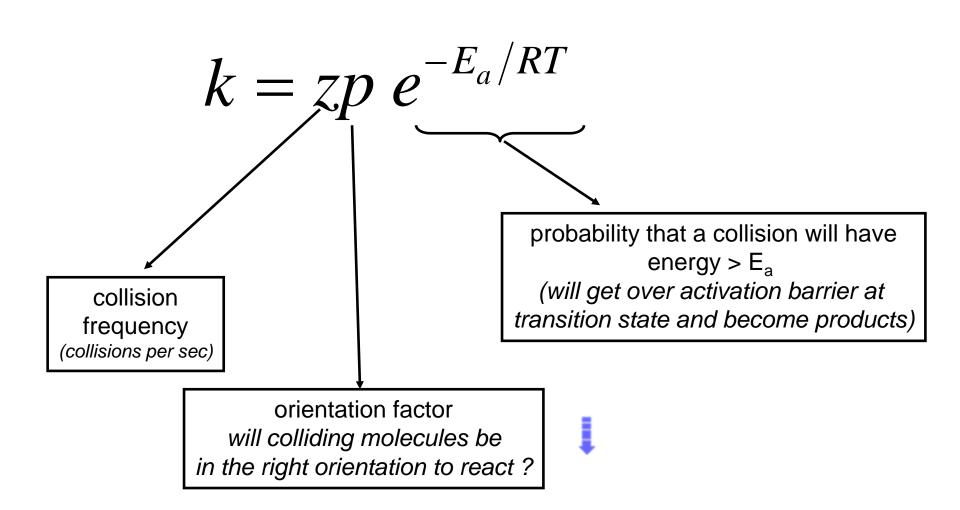
A + 2B → C MAY or MAY NOT be an elementary reaction

**TRUE** 

a multi-step mechanism for reaction may have a set of elementary reactions that coincidentally leads to the third-order rate law



- Temperature dependence of rate constant
  Catalysis

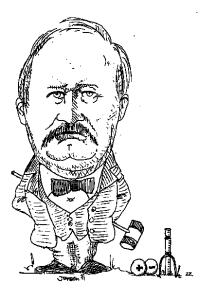


#### **Arrhenius equation**

$$k = zp e^{-E_a/RT}$$

$$k = A e^{-E_a/RT}$$

'pre exponential' factor (slight dependence on T will be ignored)



Svante August Arrhenius (19 February 1859 – 2 October 1927) was a Swedish scientist, originally a physicist, but often referred to as a chemist, and one of the founders of the science of physical chemistry.

$$\begin{split} k_{T_2} &= A \ e^{-E_a/RT_2} \\ k_{T_1} &= A \ e^{-E_a/RT_1} \\ \frac{k_{T_2}}{k_{T_1}} &= \frac{e^{-E_a/RT_2}}{e^{-E_a/RT_1}} = e^{-\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \\ k_{T_2} &= k_{T_1} e^{-\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \\ \ln k_{T_2} &= \ln k_{T_1} + \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \end{aligned} \quad \text{eqn 15.11}$$

#### Chemistry 1B SAMPLE FINAL EXAMINATION QUESTIONS

h= 
$$6.626 \times 10^{-24}$$
 J s  
c=  $3.000 \times 10^{8}$  m/s  
m<sub>e</sub> =  $9.109 \times 10^{-21}$  kg  
m<sub>p</sub> =  $1.672 \times 10^{-27}$  kg  
R= $8.3145$  JK<sup>-1</sup>mol<sup>-1</sup>  
R= $0.08206$  L atm K<sup>-1</sup>mol<sup>-1</sup>

$$\widetilde{v} = \frac{1}{\lambda} = \frac{v}{c}$$

$$\frac{1}{\lambda} = \mathbf{Z}^{2} (1.097 \times 10^{7} \,\mathrm{m}^{-1}) \left( \frac{1}{\mathbf{n}_{1}^{2}} - \frac{1}{\mathbf{n}_{2}^{2}} \right) \quad \mathbf{n}_{2} > \mathbf{n}_{1}$$

$$(\mathsf{m}\Delta \mathsf{u}) \, \Delta \mathsf{x} \geq \frac{h}{4\pi}$$

E 
$$\approx$$
 = -2.18 × 10<sup>-18</sup> J)  $\frac{Z_{eff}^2}{n^2}$   
 $r \approx (5.29 \times 10^{-12} \text{ m}) \frac{n^2}{Z_{eff}}$ 

#### wavelength range of visible light : $\lambda \approx 3.5 \times 10^{-7}$ m to $7.0 \times 10^{-7}$ m

$$k = Ae^{-E_{\pi}/RT}$$

$$\ln k = \ln A - \frac{E_{\pi}}{RT}$$

$$t_{\frac{1}{2}} = \frac{0.693}{k} \quad \text{for first-order reaction}$$

#### Energy levels of d-orbitals in octahedral crystal field:

Note: SAMPLE FINAL includes questions that are *representative* of the material, but do not include all possible topics.

bond	approximate vibrational group frequency (cm <sup>-1</sup> )
с-с	~ 1000-1400
C=C	~1600
C-O	~ 1100
C=0	~ 1800
C-N	~ 1000
C≣N	~ 2100–2200
С-Н	~ 2800-3200
N-H	~ 3300 (weak) ~1600 ( intense)
O-H	~ 3600
C-CI	~ 550-800

#### Integrated Rate Laws:

$$[A] = -kt + [A]_0$$
 zeroth-order

$$ln[A] = -kt + ln[A]_0$$
 first-order

$$\frac{1}{[A]} = kt + \frac{1}{[A]_q}$$
 second-order

#### Example (by request)

A first-order reaction with activation energy  $E_a$ =50 kJ mol<sup>-1</sup> has a rate constant of  $k_{300}$ =3.0 × 10<sup>-1</sup> sec<sup>-1</sup> at 300K.

What is the rate constant at 310K?

What is the ratio of  $k_{310}/k_{300}$ ?



#### Arrhenius equation

From Wikipedia, the free encyclopedia

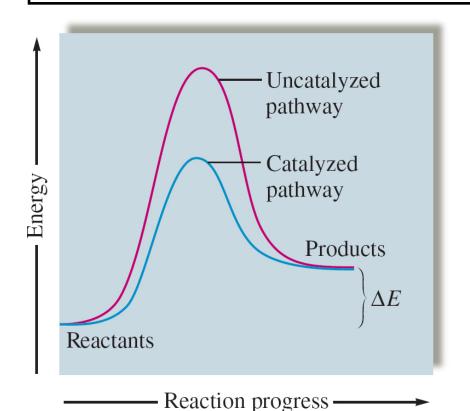
The **Arrhenius equation** is a simple, but remarkably accurate, formula for the temperature dependence of the rate constant, and therefore, rate of a chemical reaction. The equation was first proposed by the Dutch chemist J. H. van 't Hoff in 1884; five years later in 1889, the Swedish chemist Svante Arrhenius provided a physical justification and interpretation for it. Nowadays it is best seen as an empirical relationship. It can be used to model the temperature-variance of diffusion coefficients, population of crystal vacancies, creep rates, and many other thermally-induced processes/reactions.

A historically useful generalization supported by the Arrhenius equation is that, for many common chemical reactions at room temperature, the reaction rate doubles for every 10 degree Celsius increase in temperature.

$$E_a \approx 50 \text{ kJ mol}^{-1}$$
 at T=298 K

#### catalyst ?

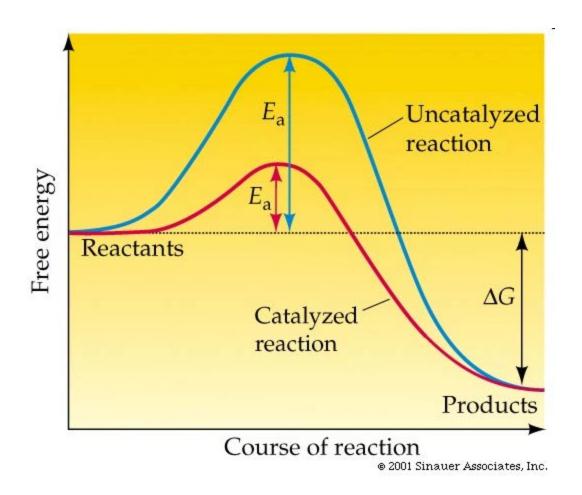
substance that increases the rate of a chemical reaction without being consumed itself





- catalysis changes the reaction pathway
- catalyzed pathway has lower E<sub>a</sub> but same

$$\Delta E = E_{products} \square E_{reactants}$$



http://www.columbia.edu/cu/biology/courses/c2005/purves6/figure06-14.jpg

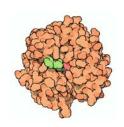
#### general types of catalysis

enzymatic catalysis

e.g. carbonic anhydrase catalyzes

$$CO_2 + H_2O \xrightarrow{\text{caranh}} HCO_3^- + H^+$$
 removing  $CO_2$  formed

in cells during metabolism



- surface (heterogeneous) catalysis
  - e.g. platinum and rhodium metallic particles in catalytic converter

converts CO, NO, N<sub>2</sub>O and NO<sub>2</sub> to CO<sub>2</sub> and N<sub>2</sub>

2NO (g) + 2CO (g) 
$$\xrightarrow{Pt (metal)}$$
 2CO<sub>2</sub> (g) + N<sub>2</sub>(g)



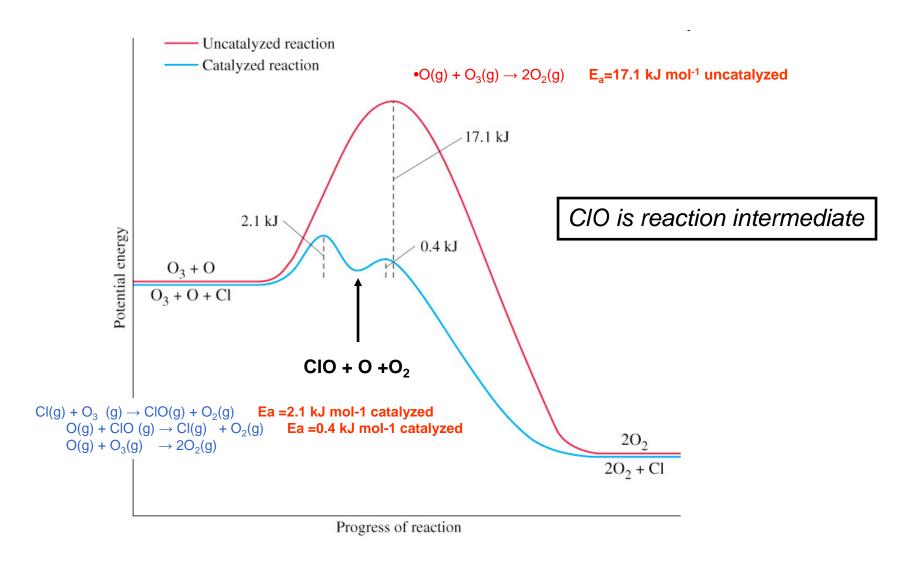
e.g. 
$$O(g) + O_3(g) \rightarrow 2O_2(g)$$

from 
$$CCl_2F_2 + h\nu \rightarrow CClF_2 + Cl^-$$

$$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$$
 Ea =2.1 kJ mol<sup>-1</sup> catalyzed

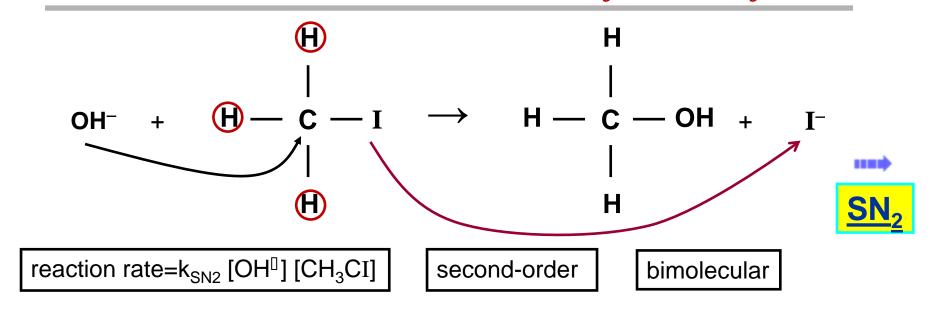
$$O(g) + ClO(g) \rightarrow Cl(g) + O_2(g)$$
 Ea =0.4 kJ mol<sup>-1</sup> catalyzed

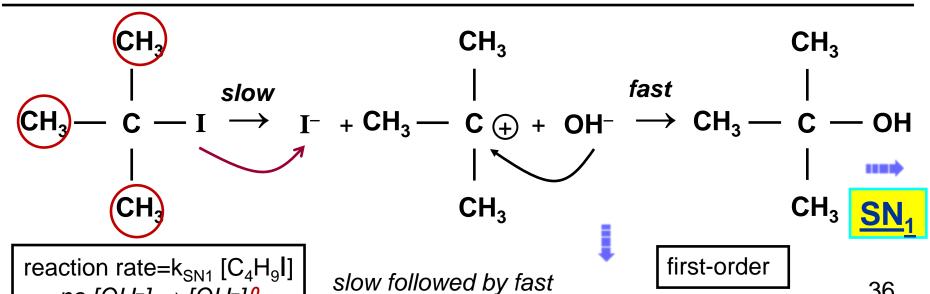




http://www.kentchemistry.com/links/Kinetics/PEDiagrams.htm

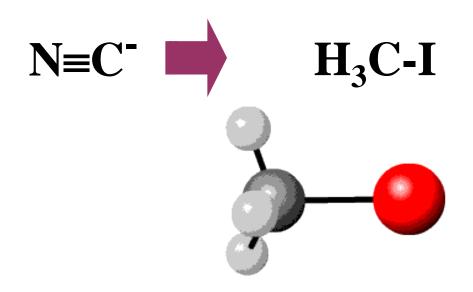
 $OH^- + H_3CI \rightarrow CH_3OH + I^- Vs$ one last example of mechanism:  $OH^- + (CH_3)CI \rightarrow (CH_3)COH + I^-$ 





no  $[OH^-] \Rightarrow [OH^-]^{\circ}$ 

36



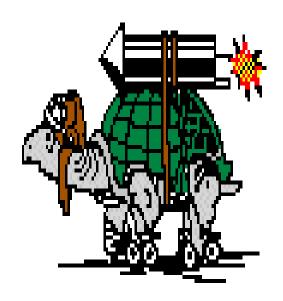
$$N \equiv C - CH_3 + I^-$$

Kinetics: How fast a reaction proceeds, and the molecular steps involved in a reaction [the mechanism of a reaction].

#### kinetic measurements: how fast will a reaction proceed





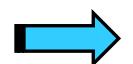




- V
- kinetics and mechanism of chemical reaction
- $\checkmark$
- energy profile and reaction coordinate
- V
- activation energy and temperature dependence of rate constant
- $\checkmark$
- catalysis

# FINIS III

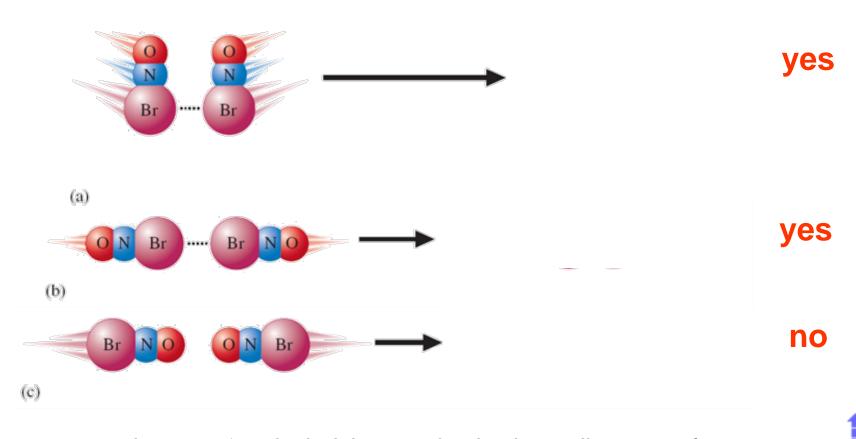
# BUT ONE MORE THING



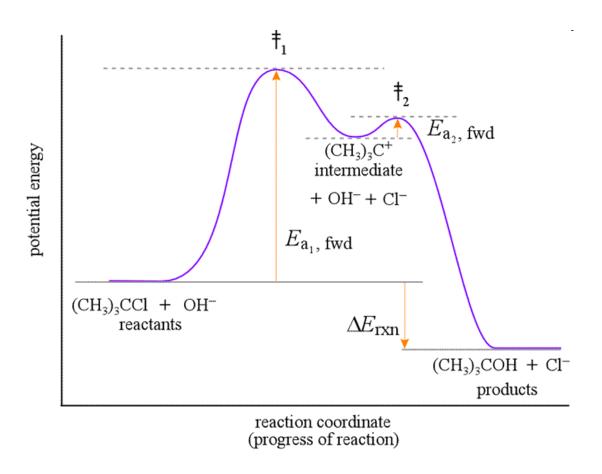
#### p the orientation factor (2 ONBr $\rightarrow$ 2NO +Br<sub>2</sub>)

what relative orientation of two ONBr molecules will lead to a reaction?

(Br-----Br bond formation)



## two-step, slow then fast, first-order with reaction intermediate HW#10 probs 67 and 68



http://guweb2.gonzaga.edu/faculty/cronk/CHEM240/images/reaction\_coordinate\_SN1.gif



#### Example (by request)

A first-order reaction with activation energy  $E_a$ =50 kJ mol<sup>-1</sup> has a rate constant of  $k_{300}$ =3.0  $\square$  10<sup>-1</sup> sec<sup>-1</sup> at 300K.

What is the rate constant at 310K?

What is the ratio of  $k_{310}/k_{300}$ ?

$$\ln k_{T} = \ln A - \frac{E_{a}}{RT}$$
1. 
$$\ln k_{310} = \ln A - \frac{E_{a}}{R(310K)}$$

2. 
$$\ln k_{300} = \ln A - \frac{E_a}{R(300K)}$$

(same A and  $E_a$ )

subtract: 1 - 2

$$\ln\left(\frac{k_{310}}{k_{300}}\right) = -\frac{E_a}{R} \left(\frac{1}{310K} - \frac{1}{300K}\right)$$

$$= -\frac{50 \times 10^3 \, J \, mol^{-1}}{8.3145 \, J \, mol^{-1} \, K^{-1}} \left(\frac{1}{310K} - \frac{1}{300K}\right) \quad note \, unitless$$

#### example continued

$$\ln\left(\frac{k_{310}}{k_{300}}\right) = -\frac{E_a}{R} \left(\frac{1}{310K} - \frac{1}{300K}\right)$$

$$= -\frac{50 \times 10^3 \, J \, mol^{-1}}{8.3145 \, J \, mol^{-1} \, K^{-1}} \left(\frac{1}{310K} - \frac{1}{300K}\right) \quad note \ unitless$$

$$\ln\left(\frac{k_{310}}{k_{300}}\right) = 0.6466$$

$$k_{310} = k_{300} \times e^{0.6466} = (3.0 \times 10^{-1} \text{sec}^{-1}) \times 1.91 = 0.574 \text{sec}^{-1}$$

$$\ln\left(\frac{k_{310}}{k_{300}}\right) = 0.6466 \implies \frac{k_{310}}{k_{300}} = 1.91 \approx 2$$



# Old adage:

raise T by  $10^{\circ}$  ( $300 \rightarrow 310$ ) double reaction rate ( $E_a \approx 50 \text{ kJ/mol}$ )

